INL/CON-07-12182
PREPRINT

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Global 2007

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September 2007

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Battelle Energy Alliance

ELECTROLYTIC REDUCTION OF SPENT NUCLEAR OXIDE FUEL – EFFECTS OF FUEL FORM AND CATHODE CONTAINMENT MATERIALS ON BENCH-SCALE OPERATIONS

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A series of four electrolytic reduction runs were performed with spent nuclear oxide fuel in a salt loading of LiCl-Li_2O at 650 ºC using a test apparatus located inside a hot cell at Idaho National Laboratory. The spent oxide fuel was irradiated UO_2 that had previously been subjected to a voloxidation process to form fine U_3O_8 particulate. Fuel particles were loaded into permeable baskets fabricated from different containment materials, i.e., stainless steel mesh, sintered stainless steel, and porous magnesia. The fuel baskets were submerged in the molten salt. A center lead that was in contact with the fuel bed was connected to a power supply as the cathode. An electric current was passed through the center lead and a submerged platinum wire, effecting the reduction of metal oxides in the fuel and the formation of oxygen gas on the platinum wire surface. Pre- and post-test salt and fuel samples were taken for analysis.

I. INTRODUCTION

An electrolytic reduction process is being developed at Idaho National Laboratory (INL) as part of an integrated process for the pyrochemical treatment of spent nuclear oxide fuel. By converting an oxide fuel to metal, the electrolytic reduction process produces a fuel form that can be subjected to existing electrorefining technology for uranium and actinide separation and recovery.[1] Indeed, the electrolytic reduction of spent nuclear oxide fuel has been demonstrated at bench-scale at INL, revealing an extent of uranium oxide reduction in excess of 98%.[2]

The pyrochemical treatment of spent nuclear oxide fuel can be enhanced by a head-end voloxidation process that facilitates the removal of spent uranium oxide fuel from its cladding. Such a process is being developed at INL and is referred to as the DEOX (Decladding by Oxidation) process. In this process, sections of clad spent nuclear oxide fuel are subjected to high temperature (greater than 450 ºC) and oxygen bearing atmospheres to convert the UO_2 fuel to U_3O_8. Oxidation of UO_2 to U_3O_8 produces a 30% volume expansion in the uranium compound, pulverizing the fuel matrix and providing a means to dislodge the fuel from its cladding.[3]

Electrolytic reduction and voloxidation processes are also being developed at the Korea Atomic Energy Research Institute (KAERI) for the treatment of oxide fuel. Indeed, KAERI has demonstrated the voloxidation and electrolytic reduction of unirradiated uranium oxide at a 10-kg scale.[4] Due to the mutual interest in advancing the pyrochemical treatment of oxide fuel, collaborative efforts between INL and KAERI ensued per International Nuclear Energy Research Initiative (INERI) projects for both voloxidation and electrolytic reduction process development.

This paper describes a series of tests that were performed at INL involving the bench-scale electrolytic reduction of spent nuclear oxide fuel that had previously been subjected to a DEOX process to form U_3O_8. One purpose of the tests was to assess the performance of U_3O_8 versus UO_2 in spent oxide fuel, while another purpose was to assess the difference in containment materials that have been used in electrolytic reduction tests at INL and KAERI. Specifically, stainless steel mesh and sintered stainless steel baskets have been used at INL for containment of uranium oxide particulate that is greater than 45 μm and less than 45 μm, respectively. Alternately, KAERI has used porous magnesia fuel baskets at bench and 10-kg scale for containment of U_3O_8 particulate that is predominantly less than 45μm.

II. EXPERIMENTAL SETUP

II.A. Equipment

The electrolytic reduction experiments were performed in a bench-scale electrochemical cell called the Hot Fuel Dissolution Apparatus (HFDA). The HFDA was located in the main cell of the INL Hot Fuel Examination Facility (HFEF) – an argon atmosphere hot cell. Crucibles and electrodes specific to the electrolytic reduction experiments were fabricated and configured in the HFDA as shown in Figure 1.

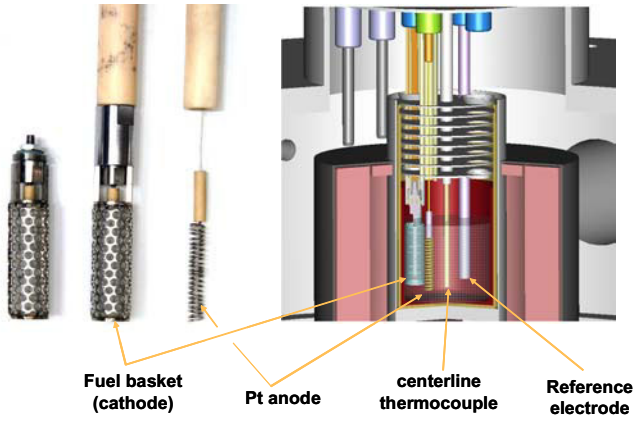

Figure 1. Sectional view of HFDA cell configuration for electrolytic reduction operations.

The HFDA houses a cylindrical steel crucible that is enveloped by an insulated resistance heated furnace with ported heat shields on the top. The heat shields contain five ports, four of which are occupied for electrolytic reduction operations as shown in Figure 1, while the vacant port is used for periodic chemical additions or salt samples. A magnesia liner was placed inside the steel crucible, which contained approximately 500 ml of molten salt. Details of the HFDA cell configuration for electrolytic reduction operations have been reported.[2]

Three different basket materials were used to contain fuel particulate in the subject electrolytic reduction tests – stainless steel mesh (depicted in Figure 1), sintered stainless steel, and porous magnesia. Both stainless steel baskets were tack-welded to an upper armature that suspended an electrically isolated stainless steel center lead. The porous magnesia baskets were configured similarly, except that the baskets were rolled pinned to the upper armature as opposed to welded. The outer diameter of the three basket types were 1.9 cm. The length between the open top and closed bottom of each of the three basket types were 5.7 cm (stainless steel mesh), 5.4 cm (sintered stainless steel) and 5.1 cm (porous magnesia). Figure 2 shows each of the three basket types.

II.B. Spent Oxide Fuel

The electrolytic reduction experiments were conducted with spent light water reactor fuel from Belgium Reactor 3 (BR3). The fuel originally contained UO_2 pellets enriched in U-235 to 8.3% in Zircaloy-4 cladding. The fuel was irradiated to a mean specific burn-up of 42 GWd/t and had decayed for nearly 26 years prior to breaching the fuel for DEOX testing. A fuel element was sectioned in 2.5 to 5.0 cm long segments and exposed to high temperature (in excess of 450 ºC) and oxidizing atmospheres (20 to 100% oxygen in argon). The pulverized particulate was separated from its cladding and subjected to various analyses. Additional details of the DEOX process have been reported.[3]

Figure 2. Stainless steel mesh, sintered stainless steel, and porous magnesia baskets (l-r) for containment of fuel particulate in HFDA experiments.

Approximately 200 grams of product from DEOX testing was acquired for the subject electrolytic reduction experiments. The material was sieved into particles greater than 45 µm and less than 45 µm. Portions of the fuel were sampled and subjected to chemical and radiochemical analysis, the results of which are shown in Table I.

TABLE I. Constituent Concentrations in Spent BR3 Fuel for Electrolytic Reduction Tests

RE (ppm)		U/TRU (ppm)		NM (ppm)		FPS (ppm)	
Nd	3800	U	787000	Zr	5900	Cs	1900
Ce	2400	Pu-239	3900	Mo	2600	Ba	2000
La	1300	Pu-240	1100	Ru-101	130	Sr	720
Pr	1200	Np-237	380	Tc	380	Rb	390
Sm	940			Pd-105	170	Te-128	59
Y	520			Rh-103	320	Eu	87

Where: RE = rare earth; U = uranium; TRU = transuranic; NM = noble metal; FPS = salt-soluble fission products

II.C. Approach

To assess the effects of fuel form and cathode containment materials on the oxide reduction process, a series of four electrolytic reduction experiments were performed with a single salt loading, as outlined in Table II.

TABLE II. Matrix of Electrolytic Reduction Tests

Run	Electrolyte	Cathode Containment Material	Fuel Particle Size
1	LiCl-1 wt% Li_2O, 650 ºC	Stainless steel mesh	> 45 µm
2	LiCl-1 wt% Li_2O, 650 ºC	Sintered stainless steel	< 45 µm
3	LiCl-1 wt% Li_2O, 650 ºC	Porous magnesia	< 45 µm
4	LiCl-3 wt% Li_2O, 650 ºC	Porous magnesia	< 45 µm

The first two runs provided investigation into the effects of fuel form on the reduction process, i.e., U_3O_8 in the subject experiments versus UO_2 from previous tests.[2] All four runs provided assessment of the performance of cathode containment materials. The third and fourth runs investigated the potential effect that Li_2O concentration in the salt may have on the reduction process.

III. RESULTS AND DISCUSSION

A molten salt solution was prepared by loading 700 g of LiCl (99.99%) in a magnesia crucible and heating it in the HFDA to 650 °C. A total of 7 g of Li_2O (99.6%) was added to the LiCl in increments to produce concentrations of 0.25, 0.5 and 1.0 wt%. Cyclic voltammetry (CV) runs were performed on the LiCl electrolyte before and after each lithium oxide addition. The CV runs utilized separate stainless steel and platinum wires (1 mm diameter) as working electrodes and a high surface area carbon steel piece as a counter electrode. The counter electrode remained in the salt throughout the series of CV runs, while the stainless steel and platinum working electrodes were introduced into the salt alternately for each of the lithium oxide concentrations. After each working electrode was immersed in the salt, a potentiostat was used to apply a potential to the working electrode at a programmed scan rate (nominally 25 mV/sec) that began at an open circuit potential and lowered (for the stainless steel working electrode) or rose (for the platinum working electrode) to a set vertex potential and then returned to the open circuit potential. The cyclic voltammagrams for the stainless steel and platinum working electrodes are shown as a combined plot in Figure 3.

Cyclic voltammetry with the stainless steel working electrode (Figure 3, left hand set of plots) identified the cathode potential relative to the Ni/NiO reference electrode at which lithium metal was generated for the varying concentrations of lithium oxide. A notable shift in the lithium formation potential was observed between the voltammagrams for 0.5 and 1 wt% lithium oxide concentrations. A similar shift in reaction potential was observed with platinum as the working electrode. Specifically, the platinum dissolution potential, as shown in Figure 3 (right hand set of plots), shifted between 0.25 and 0.5 wt% Li_2O. Cyclic voltammetry with the platinum working electrode identified the anode potentials relative to the Ni/NiO reference electrode at which oxygen ion oxidation and platinum dissolution occurred for the varying concentrations of lithium oxide.

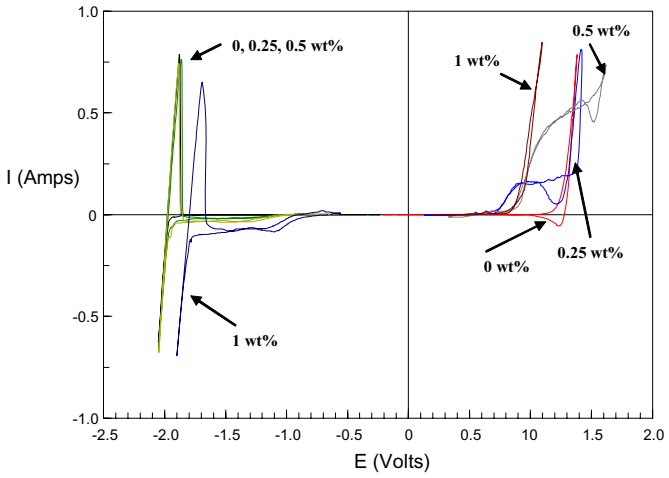

Figure 3. Cyclic voltammetry of stainless steel (left hand plots) and platinum (right hand plots) working electrodes in LiCl at 650 ºC with varying Li_2O concentrations.

A stainless steel mesh basket was loaded with 40.7 grams of 0.045 to 0.6 mm fuel particles and submerged in the LiCl – 1 wt% Li_2O electrolyte. Cyclic voltammetry with varying vertex potentials was similarly performed with the fuel basket as the working electrode, yielding a set of curves shown in Figure 4. Cyclic voltammetry with the fuel basket as the working electrode identified the cathode potentials relative to the Ni/NiO reference electrode at which uranium oxides were reduced to metal (less than -1.57 V) and at which lithium metal was generated (less than -1.78 V). Lithium metal generation in the fuel basket was consistent with preceding CV of a stainless steel wire in the same electrolyte (LiCl – 1 wt% Li_2O), which is shown as a single curve in Figure 4.

Following the CV with BR3 fuel, the lead from the stainless steel mesh basket was switched from the potentiostat to a controlled current power supply. A spiral wound platinum wire was immersed in the molten salt solution and connected to the same power supply. The power supply was energized and the current adjusted to effect the electrolytic reduction of the fuel in the basket. The platinum anode potential was monitored to ensure that the anode operated within a voltage range where the oxygen ions dissolved in the molten salt solution would

be oxidized to gas, yet the platinum anode itself would not be dissolved. After approximately 300% of the theoretical charge had been passed, the power supply was de-energized. The cathode basket was removed, sectioned, and a fuel sample was taken. Figure 5 shows a sectional view of the post-test fuel from run 1. A post-test sample of the salt was also taken. The procedure was then repeated for the other three fuel baskets, as outlined in Table II. Specifically, 40.7 g of fuel was loaded in the stainless steel mesh basket, followed by 27.8 g of fuel in the sintered stainless steel basket, 20.7 g in the first porous magnesia basket, and 20.2 g in the second porous magnesia basket.

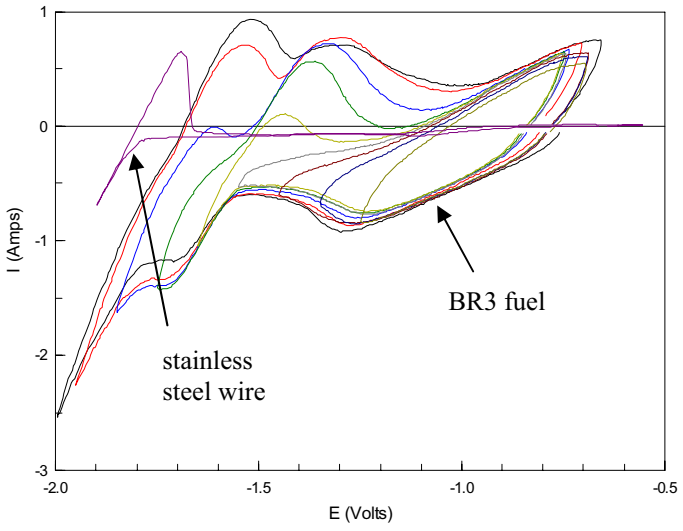

Figure 4. Cyclic voltammetry of BR3 fuel in stainless steel mesh basket (set of curves) and stainless steel wire (single curve) as working electrodes in LiCl – 1 wt% Li_2O at 650 ºC.

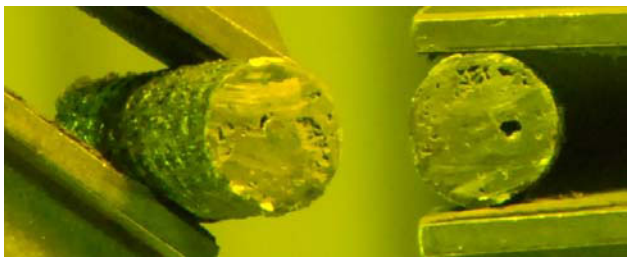

Figure 5. Post-test section of stainless steel mesh basket following electrolytic reduction of spent oxide fuel.

Since this series of electrolytic reduction tests was the first time that porous magnesia was used as a containment material, the response plot for run 3 is shown in Figure 6. The plot shows the response of the platinum anode (V_{anode}) and central basket lead ($V_{cathode}$) voltages for a controlled current ($I_{control}$) versus the Faraday charge, i.e., the ratio of applied and theoretical integrated currents. Figure 6 illustrates how the current was gradually raised to between 2 and 3 A, except for two overnight periods (0.6 to 0.7 and 2.2 to 2.3 Faraday Charge) when the current was relaxed to less than 100 mA to preclude significant reactions while the system was unattended. After approximately 290% of the theoretical charge was passed, the power supply was de-energized for run 3. Upon removal of the cathode, the porous magnesia was absent, yet a cylindrical fuel form adhered to the central cathode lead. Apparently, the porous magnesia had failed late in the run or perhaps upon removal of the basket for the fuel to remain agglomerated. The porous magnesia basket failed similarly in run 4. However, no agglomerated cylindrical fuel form was observed on the central cathode lead in run 4, as was observed in run 3.

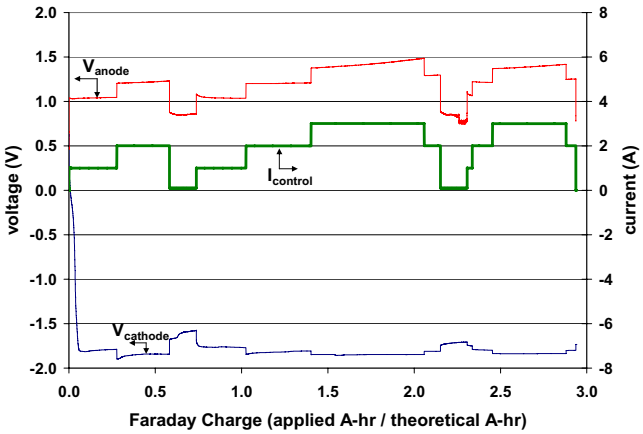

Figure 6. Response plot from electrolytic reduction of spent oxide fuel in a porous magnesia basket from run 3.

Samples of the salt and fuel were taken following each of the four runs, and a sample of the platinum anode was taken following the series of four runs. The samples have been submitted for chemical and radiochemical analyses, including Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS), Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES), and gamma spectroscopy for fission product concentration and extent of metal reduction determination. At the time of this writing the analyses have not been completed.

IV. CONCLUSIONS

A series of four electrolytic reduction runs were performed at bench scale with spent nuclear oxide fuel that had previously been converted to U_3O_8 in a DEOX process. The fuel was loaded into differing permeable baskets, including stainless steel mesh, sintered stainless

steel, and porous magnesia. Based on the cyclic voltammetry of the fuel in run 1 and the individual response plots for each of the four runs, no significant difference in the behavior of UO_2 reduction versus U_3O_8 reduction was observed. Nor was a significant difference observed in the response plots for each of the different fuel basket containment materials. The most obvious difference in the four runs was the loss of the porous magnesia at the end of each of runs 3 and 4. The loss of the porous magnesia baskets highlights a challenge in the use of ceramic materials in a remotely operated pyroprocess. Results of the chemical and radiochemical analyses of the post-test salt and fuel samples will shed further light on the effects of fuel form and cathode containment materials on these bench-scale operations.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Office of Nuclear Energy, under DOE-NE Idaho Operations Office contract DE-AC07-05ID14517. The experiments were conducted in accordance with INERI project 2005-004-K between INL and KAERI.

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